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Studies of structural and dielectric properties of $Pb(Li_{1/4}Sm_{1/4}W_{1/2})O_3$

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Abstract : The polycrystalline samples of $Pb(La_{1/4}Sm_{1/4}W_{1/2})O_3$ (hereafter PLSW), which belongs to a ferroelectric oxide family of the perovskite structure were prepared by high-temperature solid-state reaction technique. Preliminary X-ray analysis of the sample provided lattice parameters : $a = 7.0542$ Å, $b = 8.0538$ Å and $c = 12.2448$ Å and also formation of single phase compound. Detailed studies of dielectric constant and loss as a function of temperature and frequency and electrical conductivity show structural phase transition at 84°C which is quite different from the other members of the family.

Keywords : Perovskite structure, X-ray diffraction, dielectric constant, phase transition

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For the last five decades, an extensive research work have been concentrated on oxide materials of perovskite structural-type of general formula ABO_3 (A = mono or divalent, B = tri, tetra, penta or hexavalent ions) in search of materials for ferroelectric and its related devices. It has been found that some Pb-based pure/mixed oxides such as $PbTiO_3$, $PbZrO_3$, $Pb(ZrTi)O_3$, $Pb(Mg,W)O_3$, $PbHfO_3$ *etc* have shown very interesting properties useful for devices [1–8]. Extensive literature survey showed that pure or modified tungstates/molybdates of general formula, $Pb(X_{1/4}R_{1/4}W_{1/2})O_3$ (X = alkali ions, R = rare earth ions) have not been studied possibly because of high electrical conductivity of tungstates even at low temperature [9]. In order to find the existence and mechanism of the phase transition in mixed/modified lead-alkali-rare-earth tungstate or molybdate system, we have carried out systematic and extensive studies on structural, electrical, thermal and spectroscopic properties on them. In this paper, we report preliminary structural and detailed electrical (dielectric constant [ε], loss [tan δ] and electrical conductivity [σ]) properties of the $Pb(Li_{1/4}Sm_{1/4}W_{1/2})O_3$ (PLSW) compound.

The polycrystalline samples of the complex PLSW compound were synthesised using high temperature solid-state reaction techniques from the component oxides and carbonates; PbO (99.99%, Aldrich Chemical Co.), Li_2CO_3 (99%, s.d. Fine Chemical Pvt. Ltd.), Sm_2O_3 (99.99%, Indian Rare-Earth Limited) and WO_3 (AR grade, BDH, England). These oxides/carbonates were thoroughly mixed in agate mortar in air atmosphere for 5 hrs to get homogeneous mixture. The PLSW was obtained by repeated mixing and calcination at 600°C for 20 hrs. The formation of the prepared compound was checked by X-ray diffraction technique.

The fine homogeneous powder of PLSW was used to make pellets (diameter 11.2 mm and thickness 1–2 mm) at the pressure of 5×10^7 kg/cm^2 using hydraulic press and PVA binder. These pellets were sintered in air atmosphere at 622°C for 10 hrs. The X-ray diffraction (XRD) patterns of sintered pellet was obtained using X-ray powder diffractometer [Philips, counter PW-1710, Holland] with FeK_α (λ = 1.937 Å) radiation in the wide range of Bragg angle ($20° \leq 2\theta \leq 110°$). The surface morphology of the PLSW pellets was examined with the help of a Scanning Electron Microscope (SEM) [Stereocan S-180]. Some of the sintered disc samples were polished with fine emary paper to make the surfaces flat, smooth and parallel for dielectric measurements. The two flat surfaces were electroded using silver paste. Measurements of dielectric constant (ε) and loss (tan δ) were carried out on a GR-1620 AP capacitance measuring assembly as a function of frequency (f = 500 Hz – 10 KHz) at room temperature and as a function of temperature (from –150°C to 200°C) using a laboratory made three-terminal sample holder and silver paste as electrode material. The results were checked by repeating the experiments on another instrument [LCR-Hi Tester : Hioki 3530 Japan].

The sharp and single diffraction peaks of the sample (Figure 1) suggest the formation of single phase compound. All the peaks were indexed from their observed d values and then

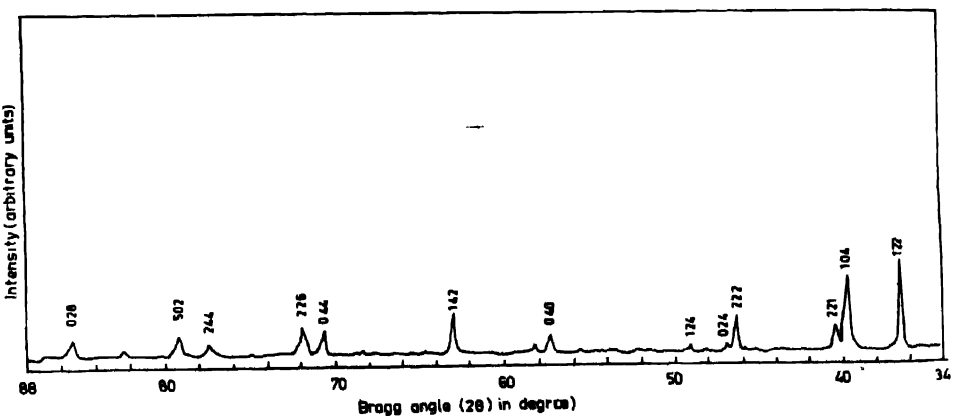

Figure 1. XRD trace of PLSW sintered pellet.

lattice parameters of a selected orthorhombic cell were determined using a standard computer program package 'powder'. The lattice parameters obtained were refined with 14 reflections

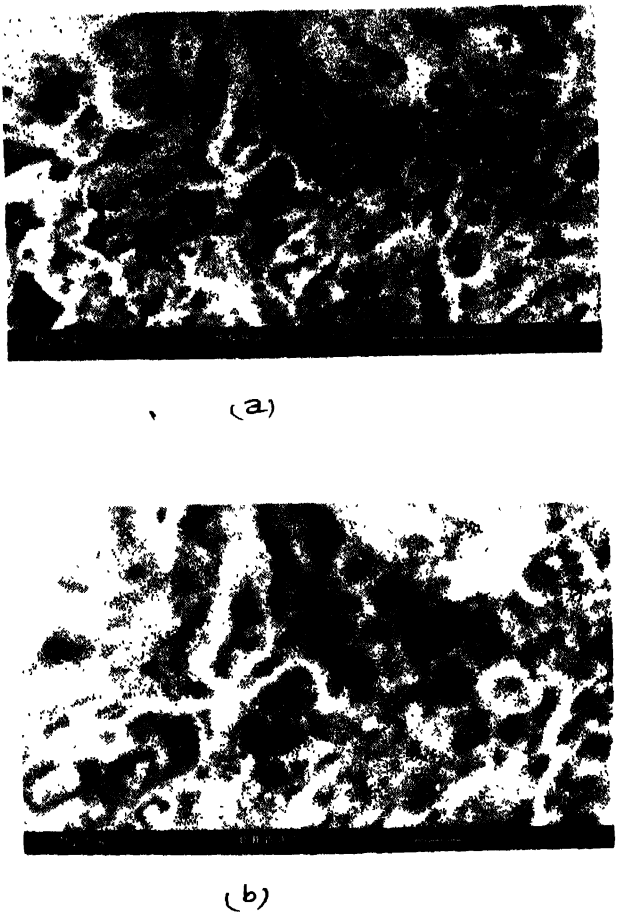

Figure 2. SEM micrograph of PLSW pellet sintered at 900°K for 2 h [(a) 10 μm, (b) 3 μm].

using least-squares method, which are : a = 7.0542 (10) Å, b = 8.0538 (10) Å and c = 12.2448 (10) Å. The comparison of observed and calculated d values (Table 1) shows a very good agreement in them suggesting the correctness of the preliminary crystal data. With the

Table 1. Comparison of observed and calculated d-values (Å) of some reflections of PLSW at room temperature.

h	k	l	d_{obs}	d_{cal}	I/I_0
1	2	2	3.0926	3.0926	100
1	0	4	2.8522	2.8522	83
2	2	1	2.8114	2.8115	26
2	2	2	2.4635	2.4550	39
0	2	4	2.4337	2.4370	13
1	2	4	2.3265	2.3275	9
0	4	0	2.0199	2.0135	17
1	4	2	1.8535	1.8584	43
0	4	4	1.6739	1.6822	30
2	2	6	1.6496	1.6497	35
2	4	4	1.5489	1.5463	15
5	0	2	1.5193	1.5216	24
0	2	8	1.4294	1.4307	22
6	0	2	1.2803	1.2801	17

limited reflections, it was not possible to determine the space group of PLSW. The linear particle size (L) of the sample obtained using the following Scherrer's equation with low and high angle of reflection [10]

$$L = \frac{0.89\,\lambda}{B_{1/2}\cos\theta} \qquad (B_{1/2} = \text{half peak width})$$

was found to be 250 Å, which is consistent and comparable with the particle size determined from particle size analyser. Figure 2a and 2b show the SEM photographs of the sample at two different magnifications.

Figure 3 shows the variation of ε and tan δ with frequency, indicating a normal behaviour of a dielectric. Figure 4 shows variation of ε and tan δ with temperature at two different frequencies [1 KHz and 10 KHz]. It was found that the value of ε was same (ε = 22) for both the frequencies at –150°C. The value of ε increases very slowly upto –10°C, and then increases very fast upto its maximum value (*i.e.*, 42.5 at 10 KHz and 95 at 1 KHz) at 84°C. These values decrease rapidly as the temperature is increased. This shows the normal behaviour of a ferroelectric material [11–13].

The ac conductivity was calculated from the formula $\sigma = \omega\varepsilon_0\varepsilon \tan \delta$, where ε_0 = vacuum dielectric constant and ω = angular frequency. The activation energy was obtained

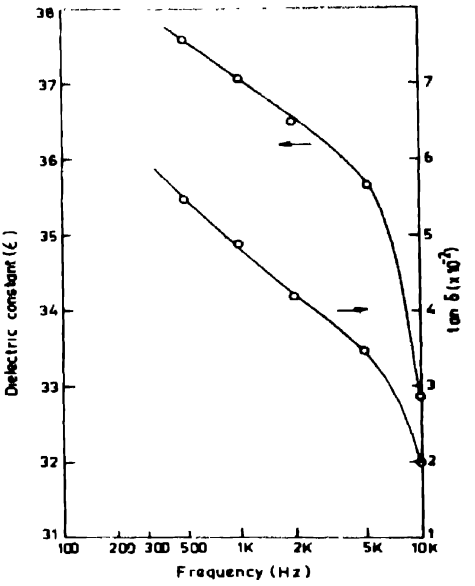

Figure 3. Variation of dielectric constant (ε) and loss (tan δ) as a function of frequency at room temperature (300°K) of PLSW

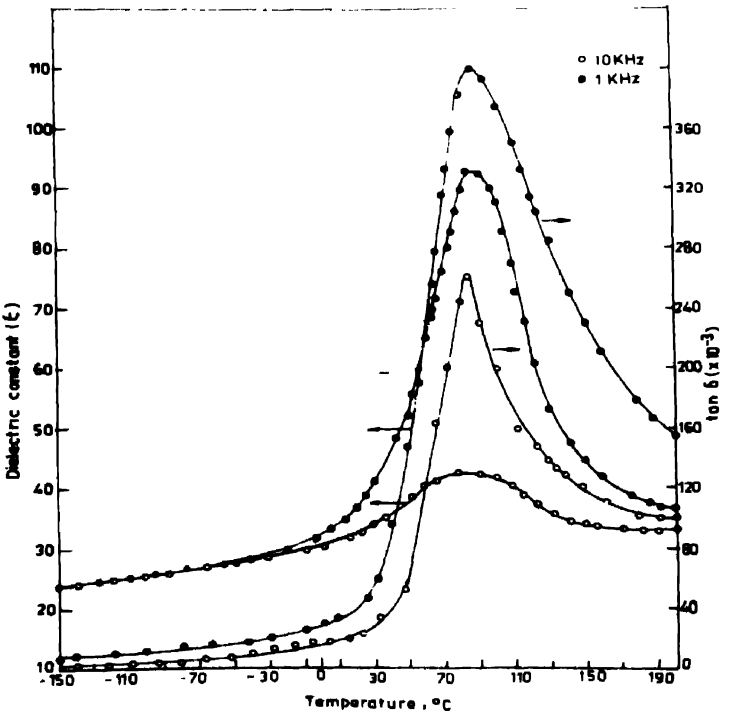

Figure 4. Variation of dielectric constant (ε) and loss (tan δ) as a function of temperature (T) at 10 KHz and 1 KHz of PLSW.,

from the graph of ln σ *vs* $\frac{1}{T}$ (Figure 5) In the room temperature to 84°C temperature region, Figure 5 gives the activation energy 0.1 ev. which is expected within this temperature region

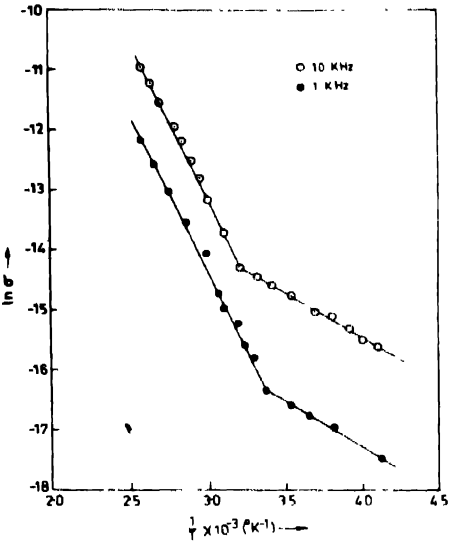

Figure 5. Variation of conductivity (ln σ) as a function of inverse of absolute temperature ($1/T$) of PLSW

for many ferroelectrics. Below room temperature, we get even smaller value of activation energy (0.06 ev). This decrease in activation energy with lowering the temperature has been observed in many ferroelectric compounds [14]. It has also been observed that if we increase the temperature of the compound above T_c (*i.e.* 84°C), the value of ln σ decreases sharply and then starts increasing [not shown in the figure]. This behaviour is also observed in some other compounds of this family [15,16]. Though the change in the slope in some of the ferroelectrics is associated with T_c, in this compound, this phenomena has not been observed.

Finally, it is concluded that the PLSW compound has orthorhombic structure at room temperature with normal ferroelectric phase transition.

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